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PP#4E1509. Trifluralin on corn. Evaluation of residue data and analytical methods, including comments on amendment of July 12, 1974.

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Coordination Branch
and Toxicology Branch, RD

Plant Protection and Quarantine Programs of the Animal and Plant Health Inspection Service, USDA, has requested the establishment of 0.05 ppm (negligible residue) tolerance for the herbicide trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) in or on field corn, grain, fodder, and forage; and fresh corn (kernels and cob) with husk removed.

Trifluralin has established tolerances of: 2 ppm in or on mung bean sprouts; 1 ppm in or on carrots; 0.2 ppm (negligible residue) on alfalfa hay; 0.05 ppm (negligible residue) in or on citrus fruits, cottonseed, curcurbits, forage legumes, fruiting vegetables, grapes, hops, leafy vegetables, nuts, peanuts, peppermint hay, root crop vegetables (except carrots), safflower seed, seed and pod vegetables, spearmint hay, stone fruits, sugar cane, sunflower seed, wheat grain, and wheat straw (Section 180.207). Food additive tolerances of 2 ppm are established for peppermint oil and spearmint oil (121.1231). A temporary tolerance for trifluralin in or on asparagus will expire August 9, 1975 [F.R., 39 (159), 29418; 1974].

Conclusions

1.(a) The nature of the trifluralin residues in plants and animals is adequately understood. Trifluralin, per se, will be the principal residue of concern.

(b) We do not expect nitrosamines of trifluralin to be present in the technical material or in soils.

(c) We do not expect nitrosobenzenes of trifluralin to be found as residues in the soil as a result of the proposed use on corn.

2. An adequate residue method with sufficient specificity and sensitivity for trifluralin is available to enforce the proposed tolerance on corn.

3.(a) Residues of trifluralin, if any, resulting from the proposed use are not likely to exceed the proposed tolerance of 0.05 ppm in or on fresh corn (kernels and cobs with husk removed), field corn grain, fodder and forage (contingent upon the suggested label changes given below under Recommendations).

(b) We do not expect trifluralin residues in the corn by-products: corn oil, corn meal and soapstock.

4. The proposed use is a category 3 situation of section 180.6(a) with respect to meat, milk, poultry, and eggs.

Recommendations

We recommend for the establishment of the proposed tolerance of trifluralin on corn contingent upon the imposition of the following label changes. The petitioner should be advised to limit the number of applications per growing season. The results of the residue field studies suggest a single application per season is appropriate. We also suggest the use be limited to the present region of witchweed contamination, i.e., North and South Carolina.

We defer to EEEB regarding the need for a crop rotation restriction for the proposed use of trifluralin on corn.

We suggest the tolerance be established/a revised Section F tolerance expression as follows: 0.05 ppm trifluralin in or on field corn grain, fodder, and forage, fresh corn (kernels and cobs) with the husks removed.

Detailed Considerations

Formulation

Trifluralin is formulated as a 4 lb./gal emulsifiable concentrate containing 44.5% active ingredient and 55.5% inert ingredients (EPA Reg. No. 1471-35). The inerts consist of [redacted]

These adjuvants are exempt from the requirements of a tolerance under Section 180.1001.

The amendment contains additional information in section A including the physical and chemical properties of trifluralin.

INERT INGREDIENT INFORMATION IS NOT INCLUDED

MANUFACTURING PROCESS INFORMATION IS NOT INCLUDED

The trifluralin manufacturing process recently submitted to the Registration Division indicates that [redacted]

As CB has stated in a previous memo on this subject and we reiterate it now to include trifluralin, this production sequence will add to little or no formation of nitrosamines (see CB memo of R.J. Hummel, 6/1/72).

Proposed Use

Trifluralin will be used for crabgrass and poorjoe control, and for pre-emergence control of witchweed in emerged corn. TREFLAN EC (4 lb./gal) will be applied at a rate of 0.75-1.0 lb. a.i./A in a subsurface layer (approximately 1 inch below the soil surface), between the rows of corn. The herbicide application will be done with special equipment designed and developed by USDA personnel at Whiteville, N.C. The machine lifts a layer of soil from between the corn rows and conveys it up a belt to the rear of the equipment. While the top 1 inch of soil is on the conveyor, TREFLAN is sprayed onto the exposed subsoil. Then the soil on the conveyor belt is redistributed over the herbicide-treated surface with a revolving spreader wheel mounted at the rear of the equipment.

Label directions state that the treatments "should be applied and incorported with special U.S.D.A. equipment". The label should be amended to include a limit to the number of applications per growing season (see Residue Data).

We also suggest the use be limited to North and South Carolina, the present region of witchweed contamination. In the event witchweed were to escape the present quarantined area in the south and migrate into the Midwest Corn Belt, we would require additional residue studies to support the proposed tolerance.

Nature of the Residue

The metabolic fate of trifluralin in plants and animals has been extensively discussed in previous reviews (see memos by T. Woodward, PP#7G0533, 10/31/66; R. Arnold and J. Wolff, PP#7F0555, 5/24/67).

Trifluralin is readily absorbed and translocated in plants. Radioactive tracer studies ($^{14}CF_3$) on carrots, peanuts, soybeans, sweet potatoes and cotton indicate the major degradation routes include a step-wise dealkylation of the aniline group and a partial or complete reduction of the nitro groups. Carboxylation of the trifluoromethyl group has also been demonstrated to a lesser degree.

There are no new metabolism data in the present proposal to elucidate the metabolic fate of trifluralin in corn, however, we believe that the degradation behavior demonstrated in the above plant studies can be extended to the proposed use.

Metabolism studies with radiolabeled trifluralin on dogs and rats indicate a complete excretionoof the radioactive values takes place within three days following administration of a single oral dose. The degradation products were also dealkylated and reduced metabolites of trifluralin and similar to that found in the plant studies. However, in vivo studies with ruminants suggest the major trifluralin metabolite was the totally reduced product, N^4,N^4-di-n-propyl-α,α,α-trifluorotoluene-3,4,5-triamine (C.M. Menzies, Metabolism of Pesticides, p. 325, 1969).

Experiments studying the formation of nitrosamines of trifluralin by nitrites present in soils were summarized and reported to CB in a conference on September 25, 1974 (re trifluralin on asparagus, PP# 4G1501). There was no evidence (<0.005 ppm) for the formation of α,α,α-trifluoro-2,6-dinitro-N-nitroso-N-propyl-p-toluidine in soil treated with 3 lb. act/A of ^{14}C-trifluralin. The analysis involves a TLC separation and a scintillation counting measurement of an extract taken from the R_f region corresponding to the nitroso derivative.

Results of studies with the formation of nitrosobenzene (α,α,α-trifluoro-2-nitroso-6-nitro-p-toluidine) were also reported in the summary. The nitrosobenzene derivative was formed by a photolytic reaction in the laboratory and found to be too unstable for use as a reference material. Since the formation of the nitrosobenzene depends upon a photolytic reaction and the proposed use involves a sub-surface soil application of trifluralin, we do not believe the nitrosobenzene will be a residue problem in this proposal.

We conclude that the metabolism of trifluralin is adequately understood. We would expect trifluralin per se, to be the residue of concern and do not expect the nitroso degradation products of trifluralin (N-nitroso or C-nitroso) to be a residue problem with the proposed use on corn.

Analytical Method

Trifluralin residue data on corn were obtained with Elanco Procedure 5801616, "Determination of Trifluralin in Agricultural Crops and Soil". This procedure is essentially the same as Method II in PAM Vol. II except that an aliquot of the initial crop extract, rather than the entire extract, is taken for clean-up and gas chromatographic analysis.

Trifluralin is extracted from corn with methanol. An aliquot of the extract is purified by liquid-liquid extraction with methylene chloride and by Florisil Florisil.

column chromatography. The final measurement is made by electron capture gas-liquid chromatography.

Validation data are submitted for the whole plant, kernel, and the cob. Trifluralin recoveries on the plant at a fortification level of 0.05 ppm ranged from 80-87%(avg. 84.2%). The controls were reported at <0.01 ppm or NDR (no detectable residue). Recoveries on the kernel ranged from 91-94% (avg. 92.5%) at the 0.05 ppm fortification level, while the recoveries on the cob at the same fortification level were reported at 86-95% (avg. 90.3%). Control values for the kernel and cob were also reported at <0.01 ppm and NDR. The recovery and control data, including the chromatograms, indicate that the analytical method is sufficiently sensitive for trifluralin residue determinations at the proposed 0.05 ppm tolerance level for corn grain and forage. We estimate the practical level of sensitivity to be apporximately 0.01 ppm.

Of the presently registered pesticides on corn, Ethion and Zineb may interfere with GLC determination of trifluralin. In those cases a TLC separation step may be incorported into the clean-up procedure prior to the gas chromatographic determination. Such a separation procedure is described in Method A of PAM Vol. II for trifluralin.

We conclude that an adequate residue method is available to enforce the proposed tolerance for trifluralin on corn.

Residue Data

Residue samples of corn were obtained which had been treated with a single subsurface layered application of trifluralin at 0.6-1.0 (1X) lb. act/A and harvested 30-90 days later. Residue results from mature kernels and cobs were also reported reflecting two applications each at 0.6 lb. act/A and at a 10 day interval between treatments. Seven field studies were conducted in the witchweed region in North and South Carolina during 1971 and 1972. Two decline curve studies are included in the data with samplings taken at 30,60, and 90 days after treatment. The samples in these studies consist of the lower (<36") and upper parts of the whole corn plant, the immature and mature kernels, and the cob. No trifluralin residues were detected at a sensitivity of 0.01 ppm. The 30 day sampling in the residue decline study corresponds to a 60 day plant maturity stage (i.e., earliest maturity for use of corn fodder and forage). Since trifluralin residues were <0.01 ppm a PHI for this use pattern will not be required.

The remaining studies include residue data for corn grain and cobs (mature). All results of treated samples and untreated checks were reported as NDR (no

detectable residue) or <0.01 ppm trifluralin residues.

No residue data are submitted for processed corn by-products, such as, corn oil, meal and soapstock, however, since the residue studies at the maximum recommended treatment rate resulted in essentially a "no residue" situation in corn grain, we will not require residue data for these fractions.

No data are submitted for sweet corn and popcorn. We have been advised via telecon with COB (L. Zink, 10/13/74) that the term "fresh corn" in the tolerance expression does not include these two items. Therefore, residue data on these items will not be required.

We conclude that residues of trifluralin in or on fresh corn (kernels and cobs with husk removed) field corn grain, fodder and forage, are not likely to exceed the proposed 0.05 ppm tolerance from the proposed use. This conclusion is contingent upon the following label restriction. The label directions should be amended to limit the trifluralin treatment to "one application per growing season", since this will approximate the conditions that were applied in the experimental field studies.

We do not expect trifluralin residues in corn oil, meal, and soapstock as a result of the proposed use.

Meat, Milk, Poultry and Eggs

The feeding studies reported in PP#7F0565 (see memo of J. Wolff, 5/29/67) indicate that up to 10 ppm of trifluralin in the diet of cows and goats would result in no detectable residues in meat and milk (<0.01 ppm). Thus, we would not expect a transfer of trifluralin residues, if any, to result from the feed use of corn grain, fodder and forage containing residues at the proposed tolerance level of 0.05 ppm.

Therefore, we conclude that the proposed use of trifluralin on corn will not result in a transfer of residues and category 180.6(a)(3) applies for meat, milk, poultry and eggs.

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